ISSN: 3049-2734
IIP : International Multidisciplinary Research Journal, Vol. 1, Issue II Oct - Dec: 2024

Synthesis and Characterization of Mono-azo Dyes: A Combinational Study.

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ABSTRACT:

Dyes are colourful compounds used to change the appearance of objects. Dyes belong to important group of compounds used to impart the desired colors. Dyes & dye intermediates are used as indicators also it is used in colouring foods, drugs, cosmetics, textiles, plastics, solvents, papers, etc. Among many different classes of dyes, azo dyes are certainly most important largest family of dyes. They contain azo group i.e., N=N linkage to two aromatic rings.

In this research work, we worked on the efficient & facile method which has been developed for the synthesis of Mono azo dyes. The nitro substituted aniline was synthesized by the reaction of substituted aniline with various coupling compounds. Product was purified by washing & recrystallization. The melting point & yield of product was recorded. During the research work we used nitro Substituted aniline because, as we know that benzene is colorless but instead of benzene, nitrobenzene has a pale-yellow color. So, here nitro group is responsible for color of nitrobenzene. That's why we use nitro substituted aniline. Correlation between structure and color of dye, effect of pH on dye was studied to verify Witt's Theory of color & constitution. We have summarized some recent synthesis of azo dye & the mechanism of azo dye. We can be applying these dyes to various type of fabrics to impart their beautiful color also we can use it in textile, fiber, printing industries, etc.

KEYWORDS:

Witt's Theory, Azo dyes, Coupling, Colour & Constitution.

INTRODUCTION:

All coloured compounds are not dyes. Dyes are coloured organic substances having the property of imparting their colour to the other substance like fabrics, leather, paper, hair, photography, etc. A dye is chemically bound to the substrate to which it is being applied. The dyes

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IIP : International Multidisciplinary Research Journal, Vol. 1, Issue II Oct - Dec: 2024

& dye intermediates are used as indicator or in colouring foods, drugs, cosmetics, textiles, plastics, solvent, paper etc. [1]

Azo dyes represent the largest production volume of dye chemistry today & their relative importance may even increase in the future. The azo dyes are synthesized by a simple method of diazotization & coupling. There are different ways to obtain the desired colour properties & yield. Most azo dyes are synthesized by diazotization of an aromatic primary amine, followed by coupling with one or more electron rich nucleophiles such as amino & hydroxy[2]. Azo dyes are generally characterized by their nitrogen-nitrogen double bond (-N=N-) & this structure affords various properties in the textile industries[3]. Azo dyes are sub-classified as monoazo, diazo, triazo & polyazo dyes according to the presence of one, two, three or more azo groups in dye molecule. So, in this research work we have synthesized various mono-azo dyes by using diazotization method followed by coupling of p,o,m-nitroaniline with α, β-naphthol etc. Mono azo dyes are the dye which contains only one azo group. Azo dye reagents are playing important role in spectral determination field to determine metal ions because of high sensitivity & selectivity [4]. A diazotization process usually prepares azo dyes & the aromatics or heterocyclic amine is converted into diazonium salt. The reaction occurs at a low temperature (0-5^{o}C) in the presence of sodium nitrite ($NaNo_2$) & acid such as HCl. The resulting diazonium complex can interact with different phenol, naphthol, forming azo dye at the end. The conventional methodology for preparing azo dyes has many drawbacks, such as the use of significant quantities of acids, toxic, costly solvents & environmentally hazardous preparation method. Therefore, new studies have tended to introduce grinding techniques as eco-friendly & safe method [5]. The grinding technique gives cunning simplicity, major selectivity, plain work lower reaction times & better yields. Azo dye compounds also have a lot of applications in industry & photodynamic therapy as well as photographic or electrophotographic systems & are dominant organic photoconductive materials [6]. The synthesized dyes are used as inkjet printing of cotton & polyamide fabrics.

Objectives of this research work:

- To prepare an azo dye from aniline or substituted aniline
- To characterize the dyes using NMR analysis.
- To verify Witt's theory of colour and Constitution.

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EXPERIMENTAL:

Materials and Instruments

Chemicals used such as nitroanilines(o/m/p), naphthol (α, β), NaOH, $NaNO_2$, HCl, NaCl were of Analytical Grade. All the synthesized products were purified, dried and identified by comparison of their physical and spectroscopic data with those of literature.

H^1NMR spectra was recorded on a BrukerDRX-400 spectrometer with tetramethylsilane as internal reference. Melting points obtained with an apparatus containing Theils tube, stand, capillary tube, burner, etc. The purity determination of the substrates and reaction monitoring were accomplished by TLC on silica-gel polygram SILG/UV 254 plates.

Preparation of Azo Dyes:

In a clean beaker, 2.8 gm (20mmol) of nitroaniline(o/m/p), 1.38gm (20mmol) of $NaNO_2$ and 6ml of H_2O was added with proper stirring & maintaining its temperature(0-5^oC) to form the Diazotised ion. Then a well stirred, cold mixture(0-5^oC) of 2.8 gm naphthol (α, β) in 10% NaOH was added to the above diazotized mixture. After stirring both the mixture thoroughly, a mixture of 6ml of H_2O & 6ml of HCl was gradually added to it. At last, the reaction mixture was heated on sand bath, 4gm NaCl was added to it and heating was continued further till the NaCl get dissolved. Then the reaction mixture was cooled, filtered, washed with dilute HCl and NaOH to remove impurities. The crude product was again washed with water and dried properly. The reaction progress was monitored by Thin Layer Chromatography (TLC) using a mixture of ethyl acetate and n-hexane (1:2) as solvent. Melting points and yields were recorded.

Schemes:

I. Synthesis of 4-(1-(3-Nitrophenyl)diazenyl)naphth-1-ol

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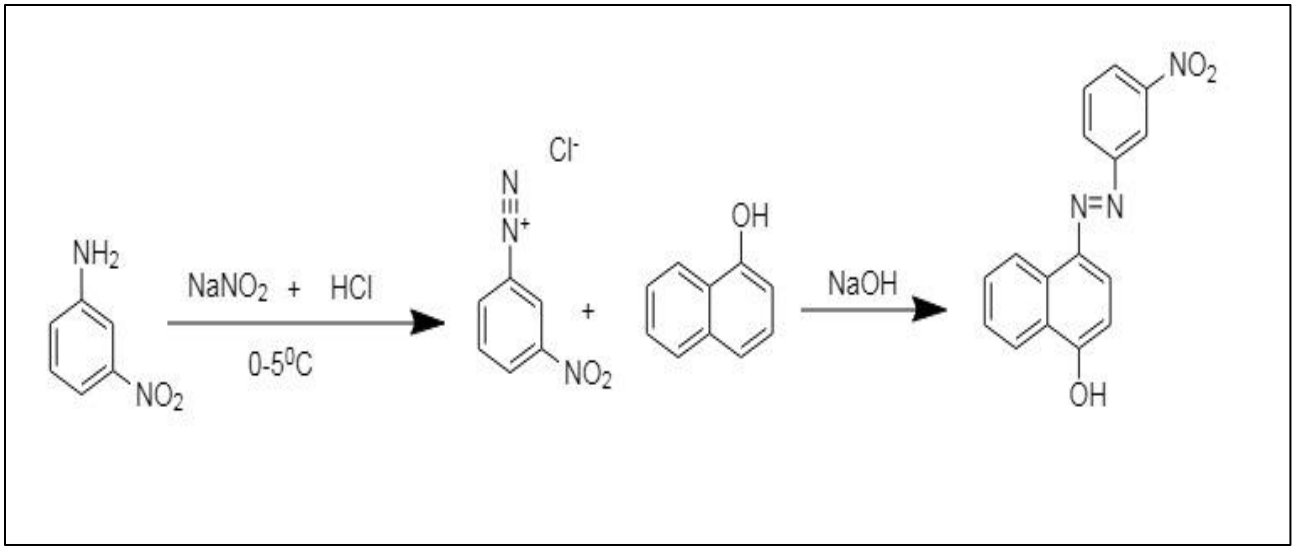
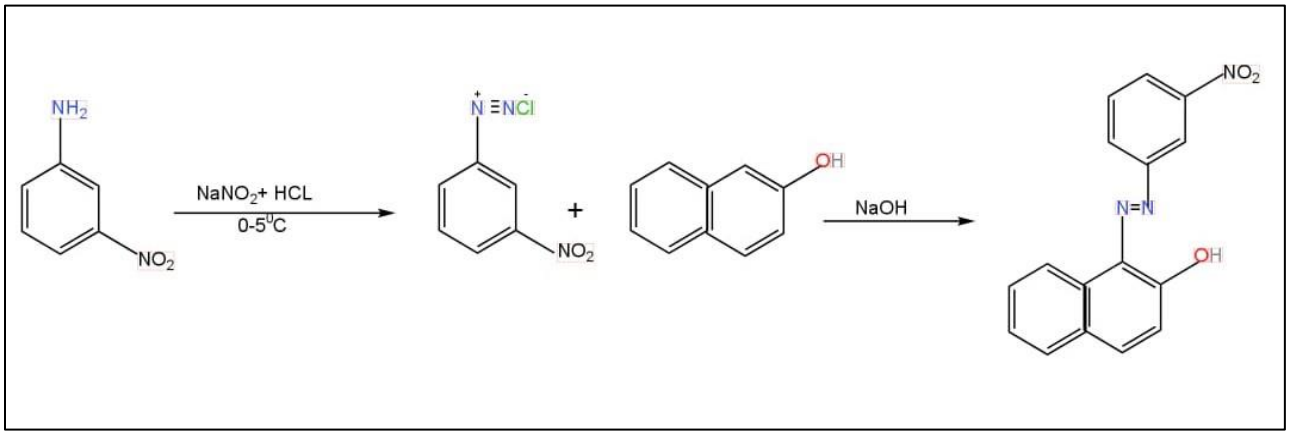
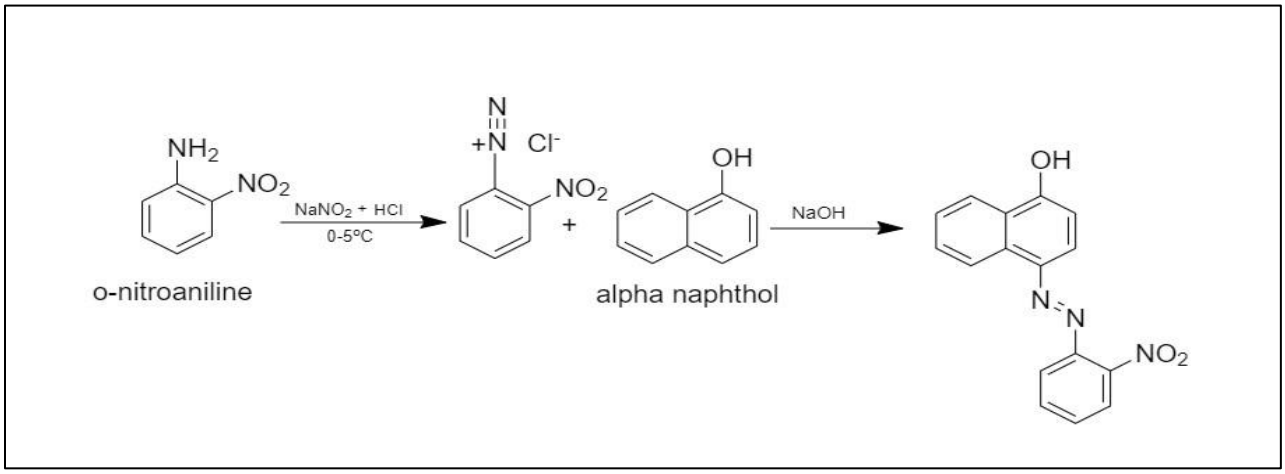


II. Synthesis of 1-(1`-(3-Nitrophenyl)diazenyl)naphth-2-ol



Synthesis of 4-(1-(2- Nitrophenyl)diazenyl)naphth-1-ol



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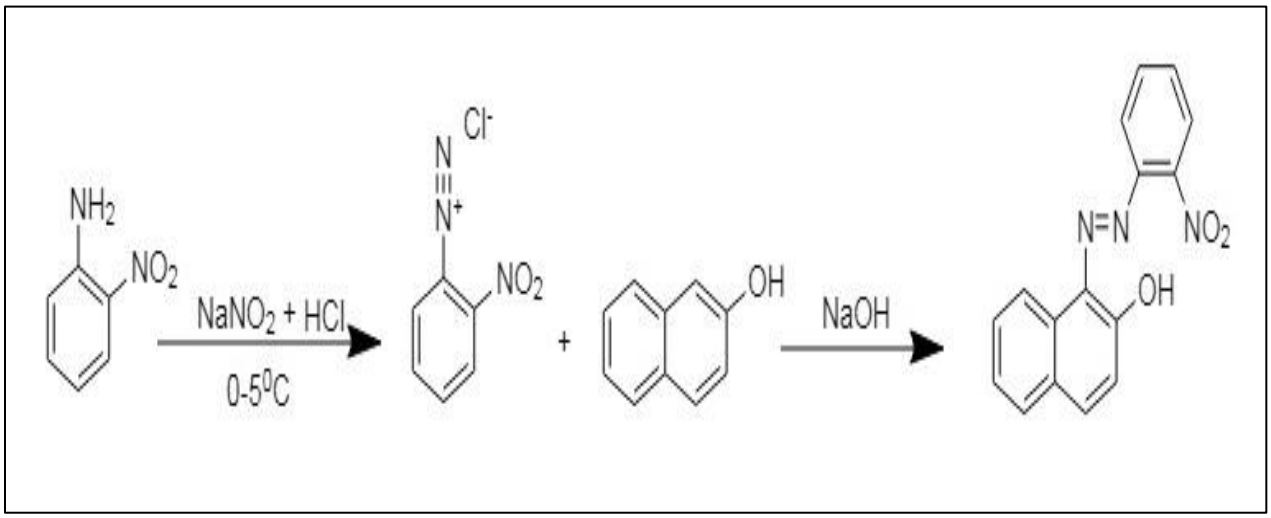
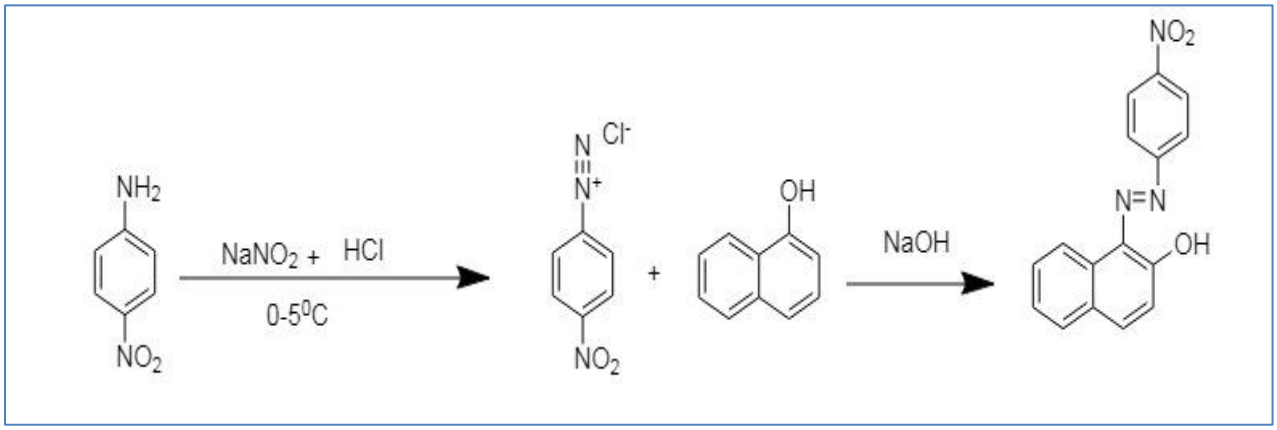
III. Synthesis of 1-(1-(2- Nitrophenyl)diazenyl)naphtha-2-ol



IV. Synthesis of 1-(1-(4-Nitrophenyl)diazenyl)naphth-2-ol



V. Synthesis of 4-(1-(4-Nitrophenyl)diazenyl)naphth-1-ol

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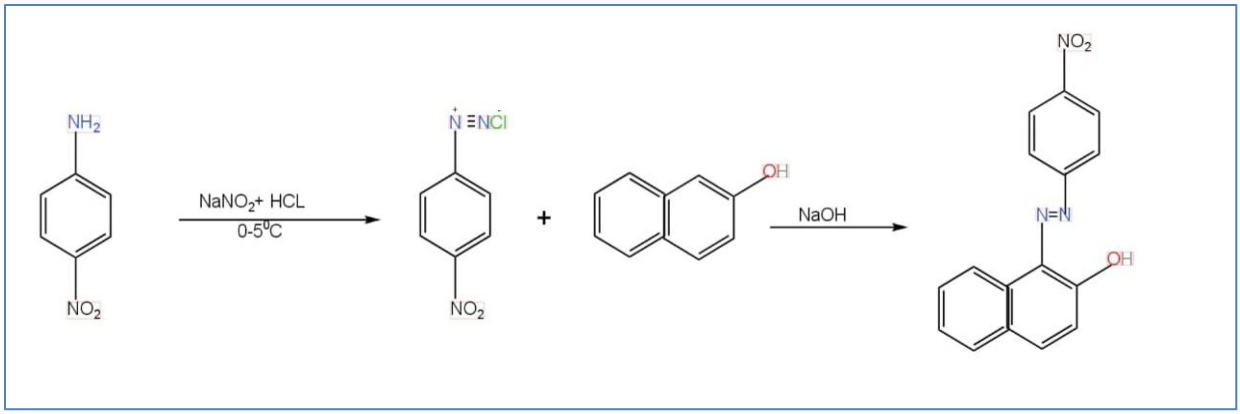

Result and discussion:

Synthesis of Benzene azo Beta naphthol is a typical experiment in organic synthesis [7]. It is also a functional group detection test for the detection of primary amine, which is commonly carried out during organic spotting. In this research work we have handled quite a number of different reagents and perform many experimental steps. The reagents that used in these experiments were hazardous. We read the safety section carefully and worked accordingly. We have encountered many observable changes throughout every experiment.

The preparation of each dye is carried out on small scale (20Mmol). The stoichiometry (1:1 mole ratio) have been kept the same. In the reaction schemes shown above, we have summarized two step process into one scheme. Monitoring of the reaction and purification is carried out by recrystallization and purity of the product is checked by physical constant (M.P.) determination and thin layer Chromatography (TLC) with proper selection of the solvent system [Ethyl acetate:n-hexane(1:2)].

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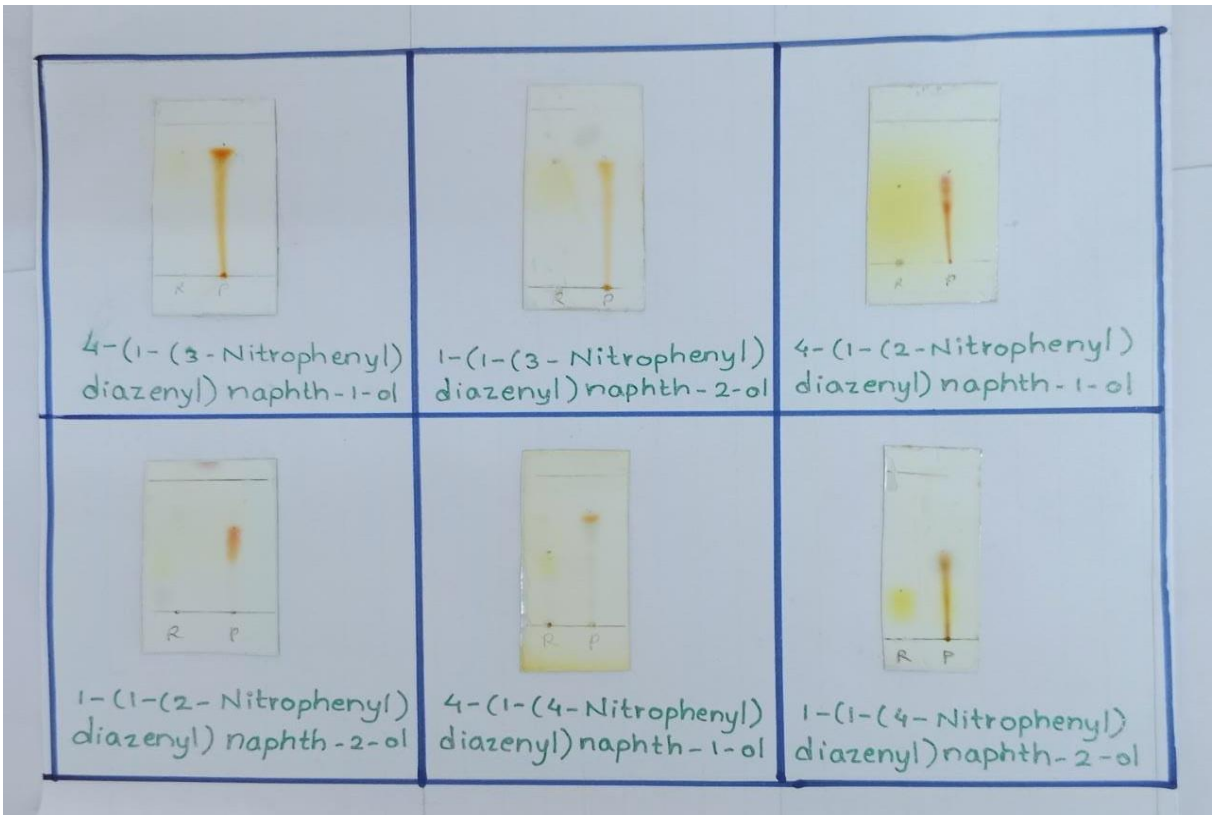

Every step in the experiment which have to be carried out carefully. The benzene diazonium salt solution is unstable and gets decomposed easily upon standing at room temperature therefore the solution should always be kept at below 10 °C and should be used as soon as it is generated (in situ preparation). The alkaline naphthalen-2-ol solution should be prepared prior to the preparation of the benzene diazonium salt solution.

Naphthalen-2-ol dissolves poorly in acidic aqueous solutions. To prevent naphthalen-2-ol from precipitating out prematurely, the addition of the acidic benzene diazonium solution to the naphthalen-2-ol solution should be slow. The mixture forms a thick paste during addition. The mixture Stirred efficiently to facilitate the reaction.

The product 1-(4-hydroxyphenylazo)-naphthalen-2-ol is a dye with an intense colour. Handle the compound with care and avoid contact with skin. Gloves are highly recommended.

Progress of the reaction is checked by Thin Layer Chromatography time to time. Products purity was checked by determining physical constant and through chromatographic techniques. Structure of the product will be confirmed through various spectroscopic techniques.

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Table 1. ***Diazotization and diazo coupling reactions of some amines with naphthols.***

Sr. No	Name of Dye	Nitroanilines	Phenol (coupling reagent	% yield	Melting point	Colour
1	4-(1-(3-Nitrophenyl)diazenyl)naphth-1-ol	m-nitroaniline	α-naphthol	63.48	248^{0}C	Bronze Brown
2	1-(1`-(3-Nitrophenyl)diazenyl)naphth-2-ol	m-nitroaniline	β-naphthol	63.10	253^{0}C	Sandstone Orange
3	4-(1-(2-Nitrophenyl)diazenyl)naphth-1-ol	o-nitroaniline	α -naphthol	61.19	249^{0}C	Sangria Red
4	1-(1-(2-Nitrophenyl)diazenyl)naphtha-2-ol	o-nitroaniline	β- naphthol	64.52	250^{0}C	Fire Orange
5	1-(1-(4-Nitrophenyl)diazenyl)naphth-2-ol	p-nitroaniline	α- naphthol	61.46	247^{0}C	Moss Green
6	4-(1-(4-Nitrophenyl)diazenyl)naphth-1-ol	p-nitroaniline	β -naphthol	66.21	245^{0}C	Dark Brown

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Dyes formed after diazo coupling reactions of various aromatic amines with α /β naphthols.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 16.03 (s, 1H), 8.52 (d, 1 H), 8.25(d, 2H), 7.89 (d, 1H), 7.73 (d, 2H), 7.58 (t, 1H), 7.42 (t, 1H), 6.80 (d, 1H), 6.78 (d, 1H) ppm.

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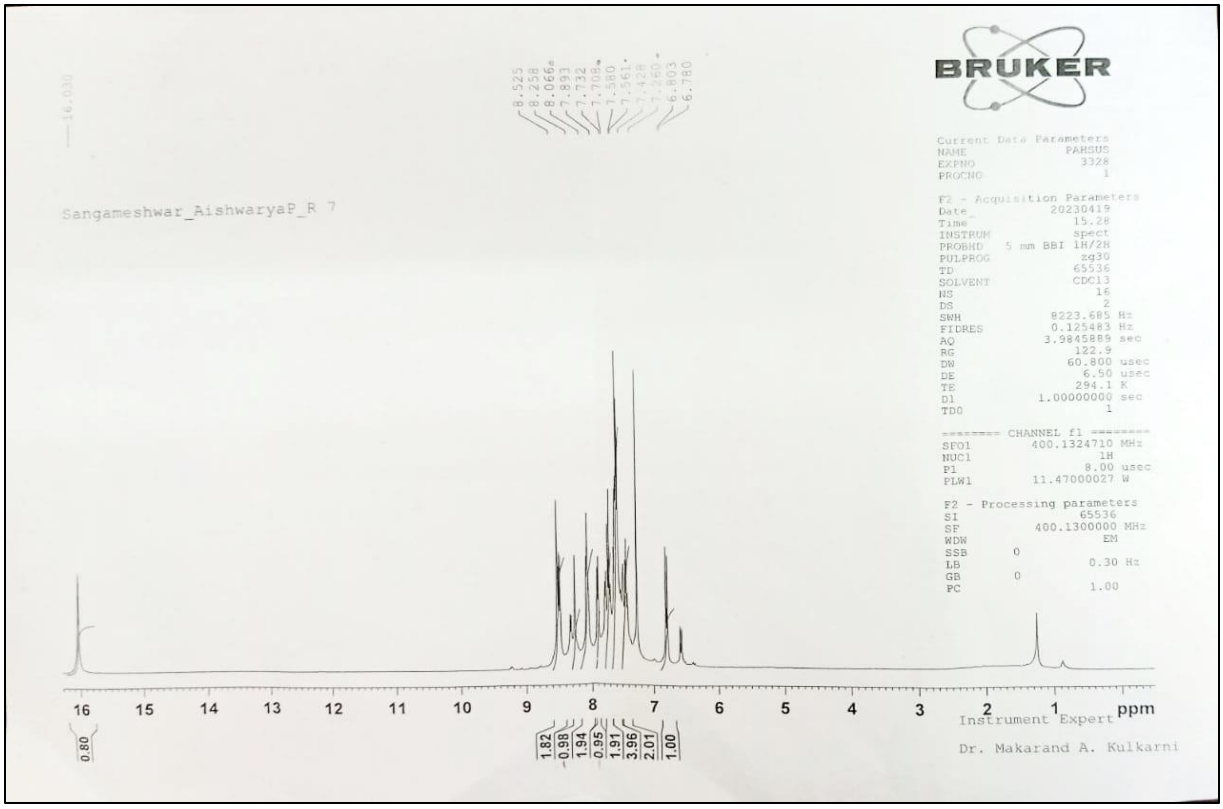

Fig 1: ^{1}H NMR spectrum of 1-(1-(3-Nitrophenyl)diazenyl)naphth-2-ol

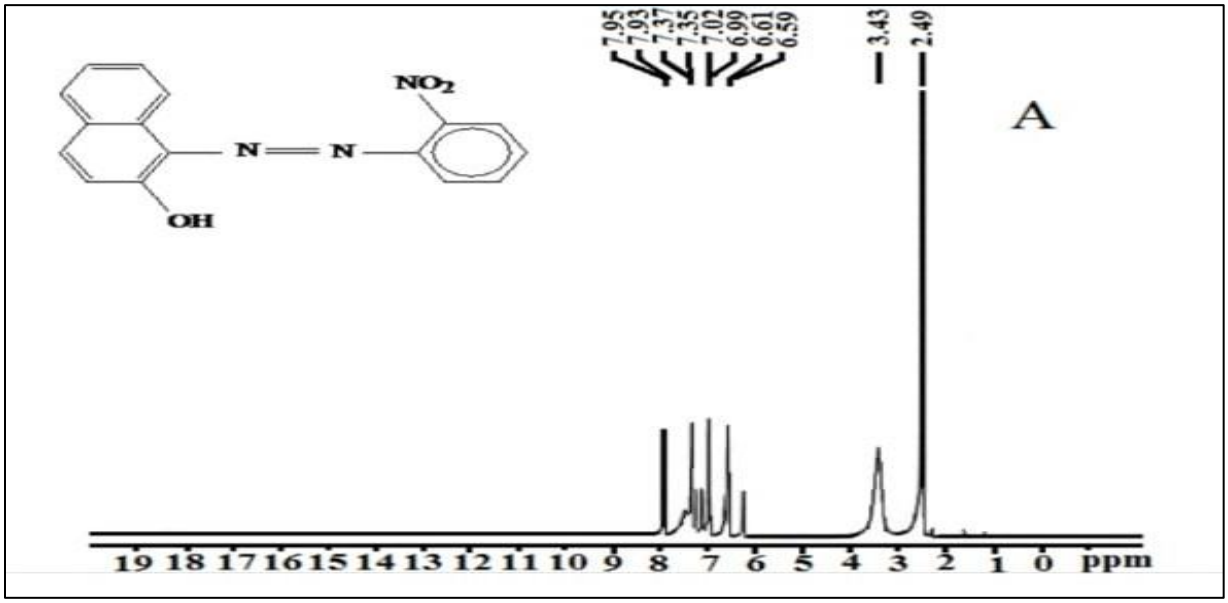

Fig.2: 1-(1-(2-^{1}H NMR spectrum Nitrophenyl)diazenyl)naphth-2-ol

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Relevance of Study:

This research work work takes a critical look at the ways of studying synthetic dyes especially monoazo dyes. It also looks at various ways of identifying the composition of azo dyes and their characterization.

Limitation of the study:

The major factors that limit the synthesis of azo dyes are the high cost of raw materials (chemicals). Another major setback is the difficulty associated with purification and the high cost of analysis, especially NMR.

Conclusion:

A series of monoazo dyes based on aniline having a nitro group with various compounds were synthesized and characterized. It was found that by changing coupling components the bathochromic and hypsochromic properties of dyes varied, which could be related to the structure of the replaced groups. Introducing electron donor and acceptor groups in the coupler has an influencing effect on the bathochromic and hypsochromic properties of the dyes. The synthesized dyes were applied on cotton fabric and gave acceptable build up and fastness properties.

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